THE PRINCIPAL MAGNETIC SUSCEPTIBILITIES OF SINGLE CRYSTALS OF RARE EARTH SALTS AT LOW TEMPERATURES. PART III—NEODYMIUM SALTS

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ABSTRACT. The principal susceptibilities of neodymium salts have been measured from room temperature down to liquid air temperature. The results are discussed in terms of Crystalline Field Theory. It is found that (1) though the mean susceptibility can be explained satisfactorily on the basis of a single cubic field even of the fourth degree, the absolute magnitude of the fourth order cubic field estimated in this manner from the magnetic data will not be correct, (2) the cubic part of the field in the various neodymium salts estimated from magnetic data on the assumption that the cubic part of the field is wholly of the fourth degree, is found to vary markedly from crystal to crystal. (3) The influence of the fourth and six degree terms of the cubic field on the Stark splitting of the rare earth ions and in crystals, and their large magnetic anisotropy go to show that the low lying energy levels as observed in absorption spectra cannot be attributed to cubic field alone. (4) The χ_1–axis of neodymium sulphate rotates by about 7° in the range studied.

INTRODUCTION

Penney and Schlapp (1932) have attempted to estimate the character and the size of the crystalline electric field acting on the Nd^{+++}ion in crystals. They find that a cubic field of fourth degree represented by $D(x^4+y^4+z^4)$ gives quite a good agreement with the measurement of $Nd_2(SO_4)_38H_2O$ by Gorter and de Haas (1931). These values of magnetic measurements give a crystalline electric field which is about three times higher than the field estimated from the magnetic measurements of Zernicke and James (1926) and St. Meyer (1925). In spite of these discrepancies one fact stands out clearly that the effective mean square moment as determined by each set of workers can be explained on the assumption of a single suitable cubic field (different for different workers) which is the same at all temperatures in the range studied.

The cubic field referred to is generally regarded as of the fourth degree and though the mean of the three principal susceptibilities can be explained satisfactorily on the basis of such a field—but the absolute magnitude of this fourth degree field as estimated by Penney and Schlapp and others (Spedding, 1937) will not be correct, since the sixth degree terms of the cubic field also influences the susceptibility of the Nd^{+++}ion, and the magnitudes of the fourth degree and six degree terms in the crystals of Nd^{+++}ions are not known.

In this communication is reported the magnetic measurements on single crystals of neodymium salts from room temperature to liquid air temperature. The results are discussed in terms of the ground level split by the cubic field of fourth and sixth degrees. The calculations of the low lying energy levels from the measurements on absorption spectra of the rare earth ions in crystals are also discussed.

EXPERIMENTAL

Crystals were grown out of aqueous solution of highly pure rare earth specimens, a gift from Professor Trombé of Paris University.

The experimental methods used in these measurements were the same as adopted in our previous measurements on cerium salts (Mookherji, 1949).

RESULTS

The results of measurements are collected in Tables I to IV. The nature of variation of magnetic anisotropy and of the square of the principal moments with absolute temperatures are shown in Figs. 1 to 5.

Notations and diamagnetic corrections used in this paper are the same as adopted in our previous paper on cerium salts.

MAGNETIC BEHAVIOUR OF Nd^{+++} ION IN FOURTH AND SIXTH DEGREE CUBIC FIELD

The ground state of the Nd^{+++} ion is $^4I_{9/2}$. The next higher level is separated from it by about 2510 cm^{-1} and hence in neodymium salts at all ordinary temperatures, the higher level will have very little influence on the magnetic properties.

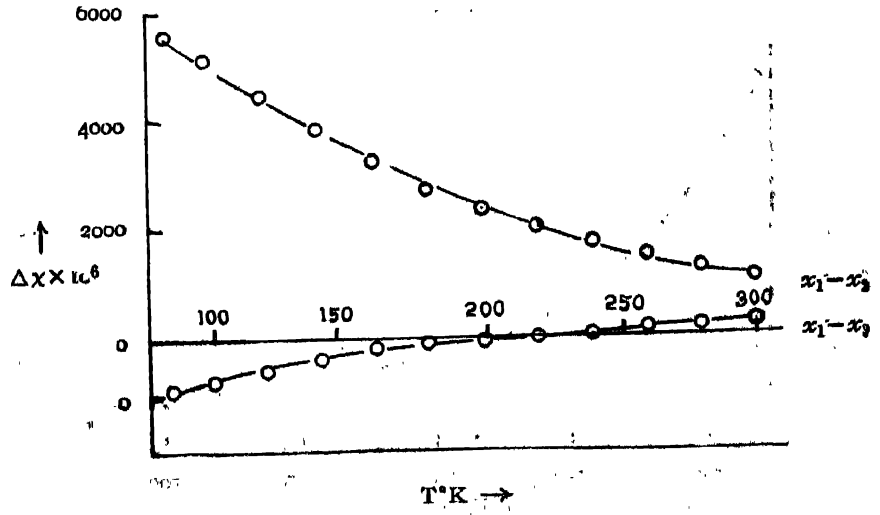

FIG. 1

$Nd_2(SO_4)_3, 8H_2O$

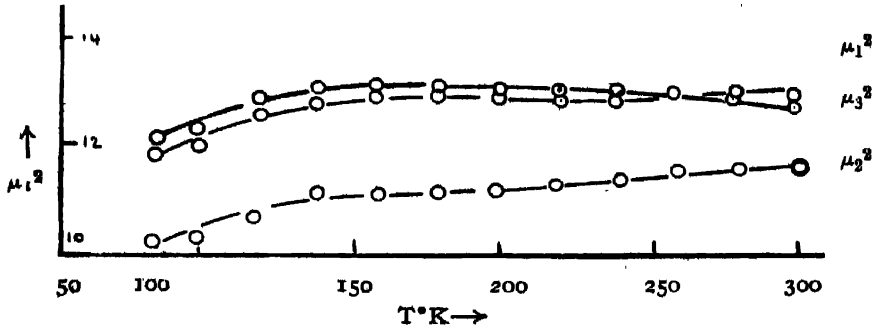

FIG. 2
$Nd_2(SO_4)_3, 8H_2O$

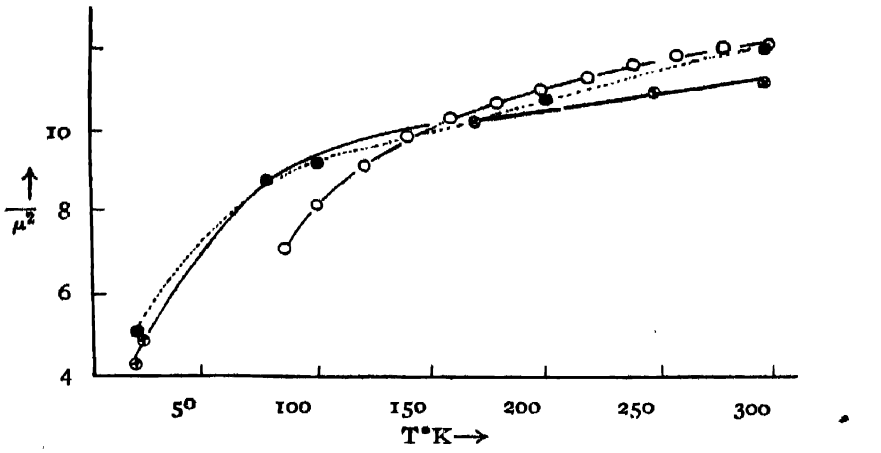

FIG. 3
$Nd_2(SO_4)_3, 8H_2O$
• — Gorter
× — Jackson
o — Author

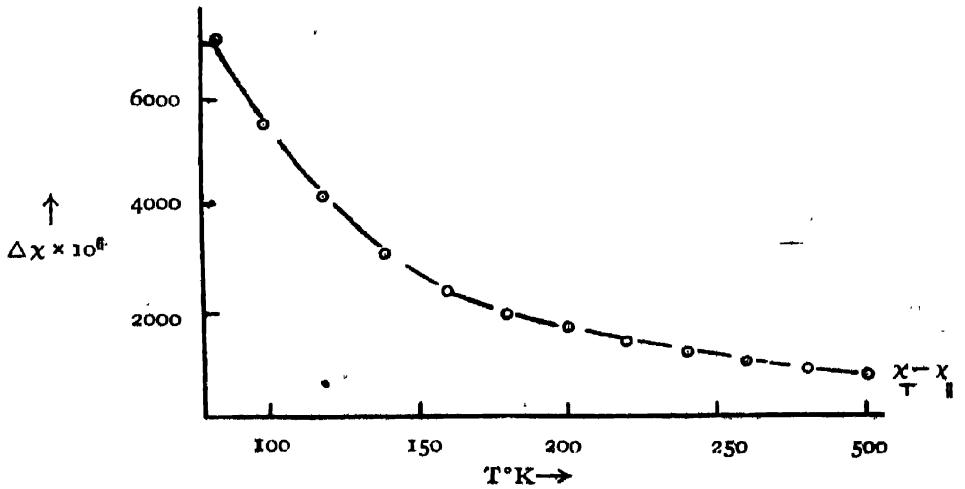

FIG. 4
$Nd_2Mg_3(NO_3)_{12}, 24H_2O$

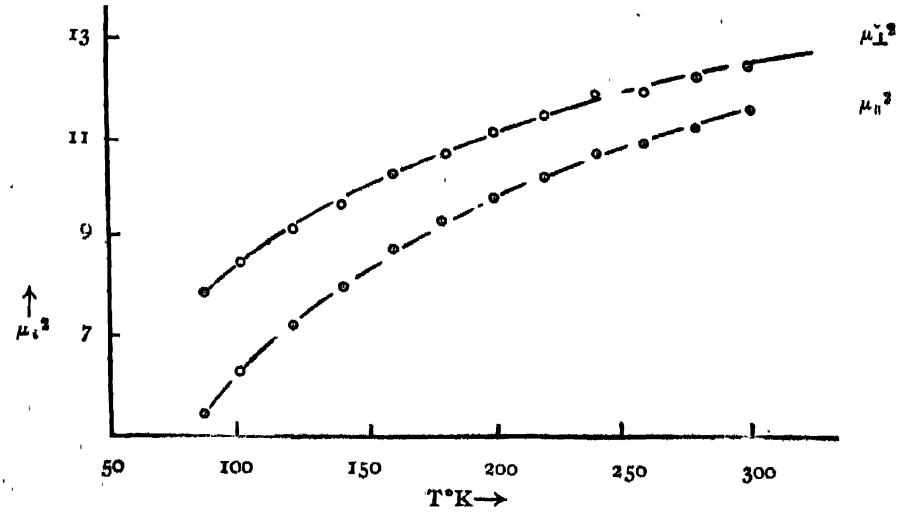

FIG. 5

$Nd_2Mg_3(NO_3)_{12}$, $24H_2O$

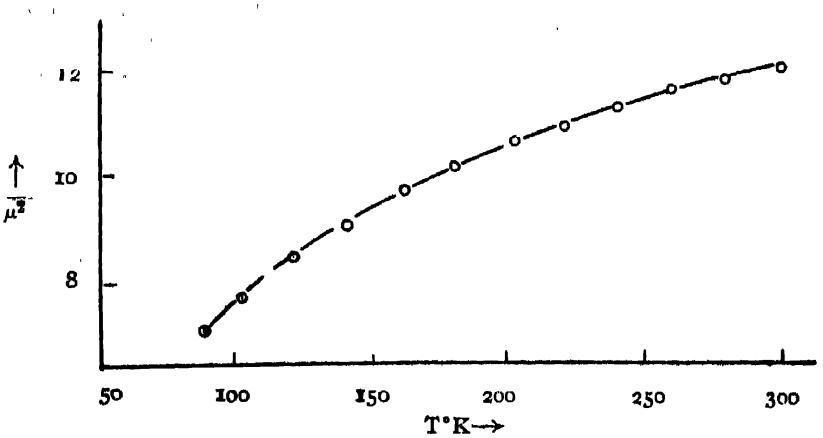

FIG. 6

$Nd_2Mg_3(NO_3)_{12}$, $24H_2O$

TABLE 1

Magnetic Anisotropy at 30°C

Crystal	Crystallographic data	Mode of suspension	Orientation in the field	$\Delta\chi$	Magnetic Anisotropy
$Nd_2(SO_4)_3$, $8H_2O$	Monoclinic prism $a:b:c$ 2.983 : 1 : 1.997 $\beta = 118°8'$	'b' axis vertical	$\theta = +14.6$	960	$\chi_1 - \chi_2 = 960$
		'a' axis vertical	'b' axis along field	188	$\chi_1 - \chi_2 = -122$
		(001) pl. hor.		1016	$\psi = 13.5$
			'b' axis along field		Cal ψ = 12.9
$Nd_2Mg_3(NO_3)_{12}$, $24H_2O$	Trigonal	Trig. Axis horizontal	Trig. Axis normal to field	636	$\chi_\perp - \chi_\parallel = 636$

TABLE II

Absolute Susceptibility along a convenient direction

Crystal	Direction along which susceptibility was measured	Temp. °C	Density of the crystal	Vol. Susceptibility	Corresponding gm. mol. sucept.	Corresponding gm. mol. sucept. at 30°C
$Nd_2(SO_4)_3, 8H_2O$	Along χ_1-axis	30.5	2.988	41.93	10110	10130
$Nd_2Mg_3(NO_3)_{12}, 24H_2O$	Normal to Trig. axis	28.0	2.185	12.67	9610	9550

Unlike cerium, and praseodymium, the splitting of the energy levels of Nd^{+++}-ion in a cubic field depends on whether the cubic field involves only the fourth degree terms or, in addition, terms of the sixth degree also. This is particularly so with the separations of the lower levels as will be seen from Table V taken from a paper by Kynch (1937) which gives the energy levels, under a cubic field involving fourth degree terms only and also under a cubic field involving both fourth degree and sixth degree terms. The magnitudes of these two groups being chosen on the basis of known distance of the negatively charged atoms surrounding the Nd^{+++}-ion in the crystal.

Hence in neodymium salts the estimate of the magnitude of the cubic part of the field from the observed mean susceptibility data will be very different according as we choose fourth degree terms alone or include sixth degree terms also. Taking, for example, $Nd_2(SO_4)_3, 8H_2O$ in which the crystalline field in the neighbourhood of Nd^{+++}-ion cannot be much different from that in the neighbourhood of Pr^{+++}-ion in the crystal of $Pr_2(SO_4)_3, 8H_2O$, since the two crystals are isomorphous, we find that, with a cubic field of the fourth degree, the energy levels will be given by (Penney and Schlapp, 1932)

$$\left.\begin{aligned} W_1 &= 20.95A \\ W_2 = W_3 &= 9.11A \\ W_4 = W_5 &= 19.59A \end{aligned}\right\} \quad (1)$$

where 'A' is a constant of the fourth degree cubic field. If the fields are exactly the same in the praseodymium and neodymium salts, A_{Nd}/a_{Pr} should be equal to 17.8 according to the calculation of Penney and Kynch (1939).

Now assuming a purely fourth degree cubic field for neodymium, the mean of the three principal susceptibilities will be given by (Penney and Schlapp, 1932)

$$\begin{aligned} \bar{\chi} = \frac{2Ng^2\beta^2}{A}\,[&(.1483e^{19.59\nu} + .239e^{-9.11\nu} - .3879e^{-20.95\nu}) \\ &+ (6.065e^{19.39\nu} + 4.031e^{-9.11\nu} + 1.68e^{-20.95\nu})] \\ &+ [2e^{19.55\nu} + 2e^{-9.11\nu} + e^{-20.95\nu}] \end{aligned} \quad (2)$$

where $\nu = A/kT$

TABLE III

Temperature variation of Magnetic Anisotropy

Crystal	Temp. °K	Suspension used for measurement		$\chi_3-\chi_1$	θ'
		'b' axis vertical	'a' axis vertical		
		$\chi_1-\chi_2$	$\chi_3-\chi_1\cos^2\theta-\chi_2\sin^2\theta$		
$Nd_2(SO_4)_3$, $8H_2O$	300	998	1040	103	+14.6
	280	1190	1160	41	14.4
	260	1410	1340	9	13.95
	240	1680	1540	− 45	13.6
	220	1980	1780	− 87	13.6
	200	2300	2040	−128	13.6
	180	2700	2360	−194	13.6
	160	3200	2810	−221	13.25
	140	3880	3270	−428	12.4
	120	4540	3730	−636	11.3
	100	5200	4260	−790	9.6
	85	5670	4660	−918	7.0
		Trigonal axis horizontal			
		$\chi_\perp-\chi_\parallel$			
$Nd_2Mg_3(NO_3)_{12}$, $24H_2O$	300	668			
	280	807			
	260	965			
	240	1150			
	220	1360			
	200	1620			
	180	1930			
	160	2360			
	140	3080			
	120	4120			
	100	5440			
	85	7040			

TABLE IV

Temperature variation of Principal Susceptibilities

Crystal and direction along which measurement was taken	Temp. °K	χ'_1	χ'_2	χ'_3	$\bar{\chi}'$	μ_1^2	μ^2_2	μ^2_3	$\bar{\mu}^2$
$Nd_2(SO_4)_3\,8H_2O$, Along χ_1–axis	300	10520	9520	10620	10220	12.73	11.52	12.89	12.36
	280	11460	10270	11500	10740	12.94	11.60	12.98	12.50
	260	12400	11000	12410	11600	13.00	11.52	13.01	12.50
	240	13400	11720	13350	11940	12.96	11.34	12.91	12.42
	220	14590	12610	14500	13900	12.94	11.19	12.86	12.33
	200	16020	13720	15890	15210	12.92	11.07	12.81	12.27
	180	17960	15250	17760	16990	13.03	11.08	12.89	12.33
	160	20270	17070	20050	19130	13.07	11.01	12.91	12.33
	140	23280	19400	22850	21840	13.14	10.95	12.91	12.33
	120	26550	22010	25910	24820	12.84	10.64	12.54	12.01
	100	30310	25110	29520	28310	12.22	10.12	11.91	11.75
	85	35350	29680	34430	33820	12.12	10.17	11.80	11.36
		$\chi_\perp$	$\chi'_\parallel$	$\bar{\chi}'$	$\mu_\perp^2$	$\mu_\parallel^2$	$\bar{\mu}^2$		
$Nd_2Mg_3(NO_3)_{12}$, $24H_2O$ Along χ_1–axis	300	10290	9620	10070	12.45	11.63	12.18		
	280	10790	9980	10520	12.18	11.15	11.84		
	260	11350	10380	11030	11.99	10.88	11.56		
	240	12260	11110	11880	11.87	10.75	11.50		
	220	12840	11840	12840	11.39	10.18	10.99		
	200	13740	12120	13200	11.08	9.772	10.64		
	180	14730	12800	14090	10.69	9.287	10.22		
	160	15880	13520	15090	10.24	8.722	9.733		
	140	17110	14030	16080	9.658	7.980	9.076		
	120	18830	14710	20400	9.722	7.120	8.450		
	100	20900	15460	26050	8.427	6.233	7.690		
	85	22900	15860	28190	7.898	5.466	7.050		

TABLE V

Only Fourth degree terms	0, 63.8 278.6 cm^{-1}
Sixth degree terms also included	0, 33.7 204.8 cm^{-1}

The value of A which fits best with experimental data is $A = -7.0$ cm^{-1}; the observed and calculated values are shown in Table VI.

TABLE VI

$A = -7.0$ cm^{-1}

Temperature °K	$\overline{\mu^2}$	
	Calculated	Observed
300	12.7	12.5
200	12.6	12.3
100	11.8	11.8
85	11.6	11.4

This value of A will correspond to $a = -.393$ for Pr^{+++} ion in the same field, whereas the actual value of 'a' for Pr^{+++} ion deduced directly from the magnetic data for $Pr_2(SO_4)_3$, $8H_2O$ is $-.585$ cm^{-1} (Mookherji, 1949).

The discrepancy is evidently due to the occurrence of the sixth degree terms in the actual fields (the second degree terms, which represent the rhombic part of the field, will not affect the mean square moment appreciably).

The discrepancy is even more striking in $Nd_2Mg_3(No_3)_{12}$, $24H_2O$ of which A calculated from the magnetic measurements on the assumption of fourth degree cubic terms alone come out as $A = -32$ cm^{-1} which will be equivalent to $a = -1.8 cm^{-1}$ for Pr^{+++} ion in the same field, whereas the value of 'a' calculated directly from the magnetic measurements on $Pr_2 Mg_3 (NO_3)_{12}$, $24H_2O$ (Mookherji, 1948) in which the crystal field is presumably the same as in $Nd_2Mg_3(NO_3)_{12}$, $24H_2O$ is $a = -0.508$ cm^{-1}.

It is clear from the foregoing discussions that while in cerium, and to a good approximation in praseodymium also, the estimate of the cubic field, assumed to be wholly of the fourth degree, from the magnetic data will be of correct magnitude, it will not be so in Nd^{+++} ion, and hence any estimate of the cubic field from the magnetic data will be unreliable in the absence of previous knowledge regarding the relative magnitudes of the two types of terms.

This is evidently the explanation of the enormous variation in the magnetic behaviour of Nd^{+++} ion in different salts of neodymium; whereas in cerium and praseodymium salts the magnetic behaviour does not show

such marked variations : this is due to the fourth degree terms of the cubic field being of nearly the same order in all salts but not the sixth degree terms.

For the octahydrated sulphate magnetic data at very low temperatures are available for the mean susceptibility from the measurements of Görter and de Haas (1931) on the powder crystal and for the principal susceptibilities from those of Jackson (1939) on single crystals. These data are given in Tables VII and VIII for comparison.

It has been observed that χ_1—axis of $Nd_2(SO_4)_3$, $8H_2O$ crystals rotate through 7 degrees as the temperature is lowered from 300°K to 85°K.

TABLE VII

T°K	300	288.5	200	100	20.4
μ^2	11.5	11.4	10.7	9.1	4.86

TABLE VIII

T°K	290	230	170	120	90	75	65	20
μ_1^2	13.36	12.96	12.40	11.47	10.54	9.78	9.39	7.06
μ_2^2	11.95	11.33	10.38	9.13	8.56	8.12	7.76	4.08
μ_3^2	12.86	12 63	11.89	10.86	9.98	9.32	8.75	5.33
μ^2	12.72	12.30	11.59	10.49	9.69	9.07	8.63	5.49

THE ABSORPTION SPECTRA IN RELATION TO THE SEPARATION OF LEVELS IN A CUBIC FIELD

Extensive measurements have been made on the absorption spectra of the rare earth salts, both in solid state and in aqueous solutions, particularly by Spedding (1937) and Freed (1931) and their collaborators. From the absorption measurements the low lying energy levels of the various rare earth ions, M^{+++} have been deduced. Now the number of these levels, and their relative separations are found to accord closely with what one should expect to occur in a cubic field of the fourth degree, and furthermore the overall separations in isomorphous salts of different rare earths are of magnitudes to be expected from nearly the same magnitude of the cubic field. These results are strikingly illustrated by the following Table IX taken from a recent paper by Penney and Kynch (1939) in which the calculated values refer to a cubic field of the fourth degree of the same magnitude in all cases, the magnitude of the field being so chosen as to give in Nd^{+++} the observed overall splitting of 260 cm^{-1}. The agreement between the observed and the calculated values is indeed very impressive.

From this close fit, Spedding concludes that the absorption measurements can give the energy levels much more accurately than the magnetic data—which is readily conceded, since the calculations from the magnetic data are based on the observed deviations of $\overline{\mu^2}$ from the Hund value and these deviations are in most cases small. For the same magnitude of the cubic field, the energy separations involve factors proportional to $Z^4_{\text{effective}} = (Z-\sigma)^4$, where Z is the nuclear charge of the paramagnetic atom, and σ is the screening constant for the $4f$ electrons responsible for the observed magnetic moment of the ion. Since the energy levels can be deduced accurately from the absorption measurements, it should be possible to utilise this data to calculate the precise values of σ, which are not so easily evaluated even from the emission spectroscopic data for the ionized atom.

TABLE IX

Ion	Levels in cm^{-1}	
	Observed	Calculated
Pr^{+++}	0, 110, 235, 500	0, 121, 207, 467
Nd^{+++}	0, 77, 260	0, 76, 260
Er^{+++}	0, 19, 41, 85	0, 19, 38, 85, 89
Dy^{+++}	0, 22, 57, 80, 112	0, 53, 57, 84, 107

In spite of the close inter-consistency of the arguments and the experimental fit, one should view with scepticism the separation of levels as deduced from the absorption spectra as representing the separation produced by a cubic field alone, and that of the fourth degree. Firstly we know that most of these salts are strongly anisotropic magnetically, and the anisotropy of the individual ions should be greater than that of the crystal, since what is observed as the anisotropy of the crystal as a whole is merely an averaged effect of the anisotropies of the differently oriented individual groups. In any case the anisotropy of the individual ions cannot be less than that of the crystal, and even such anisotropy as has been observed for the Pr^{+++} ion (Mookherji 1949) should correspond to a separation which is not much less than that produced by the cubic part of the field. Though the rhombic part of the field has little influence on the mean of the three principal susceptibilities of the crystal, its effect on the separation of the levels is quite large.

Moreover, even if the effect of the rhombic part of the field on the separation of the levels is neglected for the purpose of argument, the cubic part of the field cannot be regarded as consisting of the fourth degree terms alone. At least in the case of Nd^{+++} ion the effect of the sixth degree terms is considerable; whereas the experimental fit suggested by the data given

in Table IX is nearly as good in neodymium salts as in the salts of Pr^{+++}, for example, in which the sixth degree terms are not so effective as in Nd^{+++}.

Lastly the observed absorption spectrum of $Gd_2(SO_4)_3$, $8H_2O$ (Nutting, and Spedding, 1937), is by no means as simple as one should expect from the splitting in the crystalline field. The ground state of Gd^{+++} ion is an *S*-state, ${}^8S_{7/2}$. The splitting in the crystalline field even in strong and asymmetric ones will be quite small, of the order of a few cm^{-1}. Whereas absorption spectra suggest a complicated and widely separated set of energy levels, near the ground level. All of which show that in spite of the apparent coincidence of the energy levels, the low lying energy levels observed in absorption spectra cannot be attributed to the cubic field alone. They may be electronic levels, as influenced by vibrational levels, which in the rare earth salts may be separated by energy differences of the order of a few hundred cm^{-1}.

The evidence from specific heat data is more decisive regarding the separations of the lowest levels, but can give no more information regarding the origin of the separation of levels than absorption measurements.

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